ELECTRONIC SUPPLEMENTARY INFORMATION

Probing electrochemical phenomena in commercial pouch cells using a multimodal magnetic resonance approach

Konstantin Romanenko,*[a] Nikolai I. Avdievich [b]

[a] Université Paris-Saclay, CEA, CNRS, NIMBE, Gif-sur-Yvette, 91191, France

Email: konstantin.romanenko@cea.fr

[b] Max-Planck Institute for Biological Cybernetics, Tübingen, 72076, Germany

S1. NMR lineshape analysis

Our model is based on a qualitative lineshape assessment leading to the following empirical assumptions sufficient to describe experimental *plug-and-play* ^{7}Li NMR spectra in the SoC range from 20 to 100%:

A. Up to three distinct Li-ion environments can co-exist in the LCO cathode, giving rise to three resolved Lorentzian lines.

B. At least three distinct Li-ion environments can co-exist in the anode (Li_xC_6), giving rise to three first-order quadrupolar triplets.

C. One Li-ion environment exists in the electrolyte.

Here, we use the following spin-system indexing convention: in the cathode, s = 1, 2, 3 correspond to three singlets; in the anode, s = 4, 5, 6 correspond to three quadrupolar triplets; in the electrolyte, s = 7 corresponds to a singlet. Thus, in total, we have seven spin systems (indices s = 1 - 7), contributing to the NMR spectrum:

$$S = \Sigma_s F_s \quad \text{(S1)}$$

Multiparametric line-shape decomposition is performed with a set of Lorentzian multiplet functions F_k of the NMR frequency:

$$F_k(\omega) = \Sigma_k A_k (1 + (\omega - \omega_k)^2 R_k^2)^{-1}, \quad \text{(S2)}$$

where A_k, ω_k (Hz), and R_k are the magnitude, frequency, and reciprocal half-width-at-half - maximum (RHWHM) of a peak, respectively. The multiplicity (singlet or triplet) and frequencies of individual lines, ω_L, are determined by the residual quadrupolar couplings (RQCs):

$$\omega_L = \Omega + L Q, \quad \text{(S3)}$$

where Ω is the central frequency of the multiplet, Q is the first-order quadrupolar frequency shift, and L takes values of 0, and ±1. In accordance with assumptions (A-C), Q = 0 for spin systems 1, 2, 3, 7. Integrated intensities (I_L) of a 3/2-spin spectrum satisfy the multiplicity rule (3:4:3) and the multiplet is symmetrical with respect to Ω:

$$A_1 = A_{-1}, \quad \text{(S4)}$$

$$R_1 = R_{-1}, \quad \text{(S5)}$$

The experimental spectrum is normalized

$$S(\omega) \rightarrow S(\omega) / \Sigma_{\omega} S(\omega), \quad \text{(S6)}$$

so that:

$$\Sigma_{\omega} S(\omega) = 1, \quad \text{(S7)}$$

which also implies that

$$\Sigma_{L} I_{L} = 1. \quad \text{(S8)}$$

The NMR spectra are modeled by ten Lorentzian lines described by a total of 30 parameters (P): peak frequencies (ω), peak intensities (A) and relaxation time constants (R).

To improve the quality of data fitting, we restrict each parameter P_j within specific cutoff limits (T_{1j}, T_{2j}) via an asymptotic function of the following shape:

$$P_j = (T_{1j}\text{-}T_{2j}) \arctan(t)/\pi + 0.5(T_{1j}+T_{2j}), \quad \text{(S9)}$$

where t is a free parameter. The parameter cutoffs (T_{1j} - T_{2j}) are selected based on peak positions, intensities and linewidths of well-resolved ^{7}Li NMR signals (*e.g.*, Fig.5). For example, for A_k, ω_k, and R_k parameters of signals visible in Fig.5b (SoC > 30%), the T_1 and T_2 limits can be established within narrow margins leading to high accuracy of the fit.

S2. Battery Cells

Table S1

Cell model	OnePlus7 [1]
Cathode	LCO
Anode	G
Size (mm)	73×59×5
C (Ah)	3.6
V_{min} (V)	2.75
V_{max} (V)	4.4

LCO – Lithium Cobalt Oxide; C – nominal cell capacity; V_{min} ,V_{max} – voltage cutoff limits; G – graphite.

[1] OnePlus Technology (Shenzhen) Co., Ltd. Shenzhen (China)